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Seasonal Variations of Toxic Metal Pollution in Soil and Sediment Around Okaba Coal Mine Area, Kogi, Nigeria

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Abstract
Pollution by heavy metals presents one of the most potent threats to soil and sediment resources as well as human health. This research was carried out to determine pollution level of the heavy metals in soil and sediment and their seasonal variations in concentrations. Both dry and wet seasons soil and sediment samples were investigated for metal pollution and seasonal variations at Okaba coal mine area. The soil and sediment samples were collected in dry and wet seasons, prepared and analysed using Atomic absorption Spectrometer (Perkin Elmer model 31000), AAS. The degree of pollution and seasonal variations among metals within the sampled media were established using index of geoaccumulation (Igeo), enrichment factor (EF) and contamination factor (CF). The average values of the three (3) indices used showed that most metals under investigation have impacted on the soil and sediment in both seasons at different degrees. It was generally observed that the wet season concentration values were lower than the dry season concentrations. This could be due to dilution, dispersion, high mobility, adsorption, oxidation, hydrolysis and rapid precipitation. The concentrations of toxic metals such as Zn, Pb and Cu were higher in dry seasons than in wet seasons as a result of intense evaporation, association with sulphide minerals and their release during mining weathering and immobility in the case of Pb. Cadmium, Ni, and Fe concentrations were on the other hand higher in wet seasons than in dry seasons. This is because they were among metals not trapped in hard pan layers and thus readily released. Cadmium elevation may also be due to its association with Sphalerites which are weathered easily and dispersed. Iron (Fe) maybe as a result of co-precipitation among other factors while Pb is generally insoluble and immobile. From the study also, mean concentration of Fe in mg/l was 195.35 in dry soil and 321.89 in wet soil. Copper was 0.53 and 0.17, Zn 1.45 and 0.61, Pb 0.52 and 0.08, Ni 4.10 and 0.51 and Cd 0.55 and 1.48 in dry and wet season soils respetively. For sediment samples, the mean concentration of Fe was 608.03 and 164.12 mg/l in dry and wet season sediments respectively. Copper was 2.54 and 0.14, Zn was 2.81 and 0.54, Pb 0.56 and 0.06, Ni was 2.80 and 0.55 and Cd 0.79 and 1.12 in dry and wet season sediments respectively. In conclusion, the soil and sediment around Okaba coal mine have been polluted as a result of mining activities in both seasons. Seasonal metal variations were also observed for both media under investigation.

Keywords: *Contamination factor; Enrichment factor; Index of geo-accumulation; Okaba; Pollution.*

Introduction

Since the Homo sapiens, coal has been a source of energy. Coal may also have been used 3,000 years ago for smelting of copper (Thomas, 2002).Coal mining activities generate large amount of wastes such as spoils, waste rocks which oxidized under atmospheric conditions to release metal-rich effluents to the surrounding environments. Coal and coal waste products contain toxic metals such as As, Pb, Hg,Ni, Cd, Cu, Zn, Fe etc. These cause serious problems to the available sediments and soil bodies (*Dang, et al., 2002; Sahoo et al., 2016*). Coal mining gives rise to local subsidence/slope instability, water shortage, and sudden change in groundwater, surface water and sediment pollution. Mining activities also leads to deforestation which are hardly reversible. Dusts are generated from coal mine which are unhealthy for human survival (*Mgbemana, et al., 2011*).

Soil and sediments are substrates for organisms and both interact with water. The soil and sediment are the major sink for trace elements released during coal mining because of their high-metal scavenging potential (*Sahoo et al.,2016*). This in turn leads to degradation of chemical and microbial quality of soil and sediments and therefore a threat to humans and the environment. The negative impact of these toxic metal pollution results from their toxicity to biological processes and bioaccumulation characteristics. When these metals from coals are in solution, they form complex cations with variable oxidation states which are harmful to the environment (*Mgbemena et al.,2011*).

Open cast method of mining is in use in Okaba coal mine. This strip mining process involves removal of overburden that overlies the coal in order to expose it. The coal is scooped from the ground using very large cranes and trucks. It is an undeniable fact that coal mining and its uses have different effects on the environment. Coal mining has effect on the surrounding landscape, water courses, flora and fauna, the air, groundwater as well as social effects on the local community (Thomas 2002). Alkaline and acid mine waters have been allowed to pollute water ways and surrounding land, thereby rendering the area unusable and sterile due to the release of toxic metals. This poses major environmental hazards to the soils, sediments and humans. These levels of toxic metals have been enhanced by low pH as a result of sulphide minerals. This result to increasing bioavailability, bioaccumulation and toxicity to the environment. Groundwater is also polluted during infiltration/percolation of leached toxic metals and ions and changes in both groundwater level and direction of flow occur due to coal mining. In open pit mines, the exposure of rock to the atmosphere and hydrological cycle does produce acid mine waters. Both overburden and inter-burden, whether as infill or as spoil heaps, surface mine/waste pollute water (Thomas, 2002). Other pollutants inherent with coal mining are heavy metals and organic matter that are released into the environment during coal mining. Whether mining is underground or surface method, methane, heat, humidity and generation of fumes are common occurrences. The oxidation of coal, pyrite causes spontaneous heating and fire. Okaba coal mining has also created land degradation due to surface subsidence, solid waste, coal dumping and silting of the surface. It also disturbs the aquifer, surface water table, loss of green cover and vegetable mass. Also associated with coal mining is the disturbance and lowering of groundwater table, mineral leaching which affects groundwater quality (Thomas, 2002).

Analysis of Nigerian coal shows the presence of toxic metals such as Cd, Cu, Cr, Ni, Zn, Pb, Fe, V etc (Ogbuagu, 1999; Fagbote and Olanipekun, 2010). The presence of these metals is attributed to phyrites minerals, base deposits and other mining activities which must be removed from the soil and sediments for the safety of human health and sustainable development. This current study is to therefore establish the degrees, distribution and categorization of the soil and sediment pollution with these toxic metals and the seasonal variations of the metals within the sample media.

Geology

The large deposits of coal in Nigeria are within the Benue Trough (*Obaje et al; 1994*). The Anambra Basin in the Lower Benue Trough is a major coal producing basin in Nigeria. The coals in Nigeria are found in the Mamu and Nsukka Formations, the Lower and Upper Maastrichtian to Danian respectively (Figure 1). The coal in Okaba area of study is found in the Mamu Formation (Obianuju, 2005; Okunlola and Idowu, 2012), intercalated with shales/carbonates materials, siltstones, mudstones and sandstones (*Ogala et al., 2009*). The stratigraphic succession from bottom to top in Anambra basin is: Nkporo shales (Campanian); Mamau Formation (Lower coal measures), Ajali sandstones and the Nsukka Formation (Coker, 2003; Obianuju, 2005; Okunlola and Idowu, 2012) (Figure 1).

PERIOD/AGE		FORMATION
Tertiary	Eocene	Bende/Ameki Formation
	Palaeocene	Imo Shale Group
Cretaceous	Maastrichian - Palaeocene	Nsukka Formation
	Maastrichian	Ajali Formation Mamu Formation
	Campanian - Maastrichian	Enugu/Nkporo /Owelli Formation
	Santonian	XXXXXXXXXXXXXXXXXXXXXXXX

XXXXXXX Major Unconformity

Fig. 1: Stratigraphic sequence of Anambra Basin (after Ogala *et al.*, 2009).

Materials and Methods

Sample Collection

Top soil samples from 0cm to 20cm depths were collected around the study area with the aid of hand auger (Figure 2). Stainless spoon was used to scoop the soil. Soils from 0cm to 20cm depths were homogenized in a steel bowl and sub samples were collected into well labeled polyethylene sample containers and transported to the laboratory for analysis. Sediment samples were collected from 5cm layer of the surface using Ekman grab sampler (Figure 3). The sediments collected were homogenized using a stainless spoon and subsequently stored in a well labeled polyethylene container washed previously with a solution of 10% HCl (US EPA, 1996; 2007).

Sample Preparation and Analysis

The soil and sediment samples were spread in open air and allowed to dry till constant weight was achieved. The samples were light rolled, powdered with porcelain pestle in a mortar. The samples were screened through a 2mm nylon sieve to obtain the <2mm fractions. About 1.5gm each of the <2mm fractions were digested in microwave model 7295 and analysed using technique suggested in US EPA (1996; 2007) method 3050B, consisting of an acid mixture of HNO_3.The digestion was completed with the addition of H_2O_2. The solution was filtered after cooling, diluted with distilled water to

50ml dilution factor. A reference material was used and analysed at the beginning and end of each batch of sample for accuracy and precision of analytical method. Recovery rate ranged between 95% and 100%. Detection limit was ± 0.02mg/l. All samples were analysed in the Faculty of Agriculture laboratory, Kogi State University, Anyigba using AAS (Perkin Elmer model 31000). Standard solutions at different concentrations of recognized grades were also used. Samples were analysed in duplicates (US EPA, 1996; 2007).

Data Evaluation Methods

(I) *Contamination Factor* **(CF).** The level of soil or sediment contamination is expressed in terms of contamination factor calculated as: CF = metal content in soil or sediment divided by background value of the metal (Hakanson, 1980).
Where: CF<1 = low contamination;
1 ≥CF ≥3 moderate contamination;
3 ≥CF ≥6 considerable contamination;
CF > 6 very high contamination (Hakanson, 1980; Harikumar and Jisha, 2010)

(ii) *Index of geo-accumulation* **(Igeo)** The I_{geo} = log2 [(C_m)/ (1.5* C_p)] as proposed by Mueller, 1979 has been used to evaluate the degree of toxic metal pollution in soil and sediment.
Where C_m = measured concentration of metal (m) in soil or sediment;
C_p = control point concentration of metal;
1.5 = a factor for possible variations in reference concentration due to lithologic differences.

(iii) Geo-accumulation indices (Mueller, 1979) of pollution intensity of heavy metal have seven descriptive classes of contamination based on increasing numerical value of Igeo as follows.
< 0 = practically uncontaminated;
0-1= uncontaminated to slightly contaminated;
1-2= moderately contaminated;
2-3= moderately to highly contaminated,
3-4= highly contaminated;
4-5= highly to very highly contaminated;
>5 =very highly to strongly contaminated
The latter is an open-end class and includes values above 5. Igeo of 6 is indicative of 100-fold enrichment of a metal with respect to the baseline value (*Mohiuddin et al., 2010*)

(iv) **Enrichment factor (EF).** This was computed relative to the abundance of species in same material to that found in an unpolluted area with similar geology. The EF is expressed as X/Fe (soil or sediment) = X/Fe (earth's crust) (Sutherland 2000).
where X= metal studied and X/Fe is the ratio of concentration of element in X to iron (Fe).
Enrichment factor is used to differentiate between metals from anthropogenic activities and those from natural sources to assess the degree of anthropogenic influence (Charkravarty and Patgiri, 2009).

Five (5) contamination categories were recognized (Sutherland, 2000).
Where EF ≤1=background concentration;
EF 1-2= deficiency to minimal enrichment;
EF 2- 5= moderate enrichment;
EF 5- 20= significant enrichment;
EF 20- 40= very high enrichment;
EF > 40= extremely high enrichment.

As the EF increases, the contributions due to anthropogenic origin also increase (Sutherland, 2000). The control point values were obtained far away from the influence of coal mining but similar geology and unpolluted was used for all the indices.

Results and Discussion

Metal Concentration in Soil and Sediments at both Seasons

Tables 1a and b are the summary of soil data for both seasons. Fe has the highest mean of 195.35mg/l, followed by Na (141.734mg/l), K (31.65mg/l) while the least mean of 0.52mg/l was for lead in dry season. Ni has the highest mean of 4.10mg/l, followed by 1.45mg/l for Zn among the toxic metals and least was Pb (0.52mg/l). Every other index was highest for Fe (Table 1a). In the wet season data, Fe has the highest mean of 321.89mg/l, followed by K and Ca with values of 38.02mg/l and 28.21mg/l respectively. Of all the toxic metals, Cd has the highest value of 1.48mg/l, followed by Zn with a value of 0.61mg/l and Ni (0.51mg/l). Overwhelmingly, Fe is the most dominant element in the area in both seasons. Except for K, Mg, Fe and Cd, all other elements recorded lower concentrations during wet season than in the dry season (Tables 1a and b).

The sand and clay proportions were higher in Okaba. Organic matter content was low and pH of the area was acidic (Table 2).

Table 1a: Summary statistics of Okaba dry season soil samples (mg/l)

Variables	Minimum	Maximum	Mean	Std. Deviation	t- square	95% Confidence Interval of the Difference Lower	Upper	Average Control point value
Na	80.56	211.63	141.734	48.65	9.66	109.06	174.42	36.73
K	20.72	45.67	31.65	8.08	13.00	26.23	37.08	15.25
Ca	19.32	42.72	30.87	6.87	14.90	26.26	35.49	30.41
Mg	.02	5.68	1.92	1.99	3.20	.58	3.26	4.12
Fe	89.47	507.50	195.35	121.36	5.34	113.82	276.89	86.52
Cu	.23	1.31	.53	.34	5.22	.31	.76	.18
Zn	.22	2.39	1.45	.63	7.60	1.02	1.87	.54
Pb	.32	.94	.52	.17	9.99	.40	.63	.05
Ni	1.31	5.83	4.10	1.63	8.34	3.00	5.19	.86
Cd	.12	.84	.55	.21	8.92	.42	.69	.35

Source: (Ameh et al., 2014)

Table 1b: Summary statistics of Okaba wet season soils (mg/l)

Variables	Minimum	Maximum	Mean	Std. Deviation	t-square	95% Confidence Interval of the Difference Lower	Upper	Average control point value
Na	14.06	17.46	15.50	1.11	41.91	14.65	16.36	62.61
K	8.12	63.27	38.02	18.44	6.19	23.85	52.19	36.72
Ca	21.20	31.52	28.21	3.96	21.39	25.17	31.25	23.07
Mg	2.86	3.41	3.10	.18	52.49	2.96	3.23	3.01
Fe	144.25	465.00	321.89	105.69	9.14	240.65	403.13	71.00
Cu	.01	.31	.17	.10	5.10	.09	.24	.39
Zn	.22	1.00	.61	.24	7.44	.42	.79	.38
Pb	.01	.23	.08	.067	3.72	.03	.14	.11
Ni	.01	.88	.51	.23	6.67	.33	.69	.04
Cd	.78	2.05	1.48	.54	8.28	1.10	1.89	.02

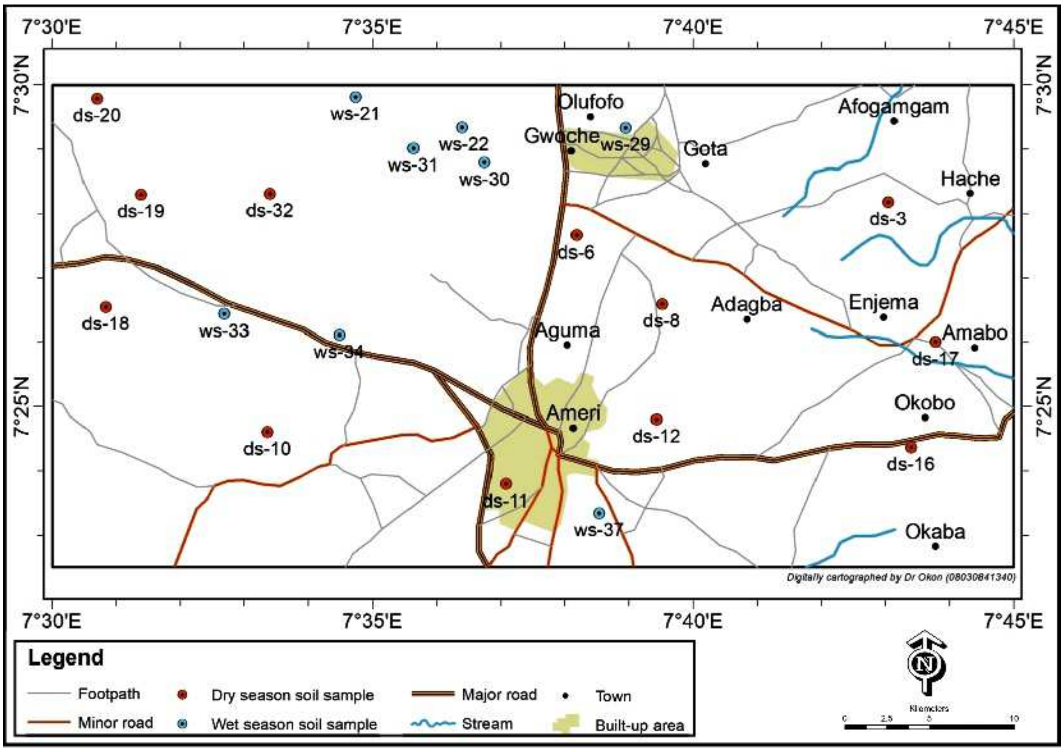

Fig. 2: Soil sample map.

Table 2: Average soil properties in Okaba coal mine

Sand %	38.21
Cay %	39.52
Silt%	25.87
Ec	2.86
pH	6.38
OM%	3.41
Temperature	27°C

Ecological Indices for Soil at both Seasons

Coal mining activities releases toxic metals into the soil. From the result of the Igeo, the soil showed higher concentrations of metals in soil around the mines than the control point values.

during wet season. Iron (Fe) was moderately to unpolluted (Igeo of 1.5), Ni was moderately polluted (Igeo of 2.58) and Cd had the highest Igeo of 5.52 which means very highly polluted soil with Cd (Table 3b).

Comparing both season soils (Tables 3a and b), Cu and Zn have below background Igeo in wet season but unpolluted in dry season soil. Iron (Fe) was unpolluted in dry season but moderately to unpolluted in wet season soil. In dry season soil, Ni and Cd were both moderately to unpolluted in the soil but in wet season, the soil was moderately polluted with Ni. In the same wet season, Cd was very highly polluted in the soil. These results showed that the metals were not only higher in soil around the coal mine area but varied between dry and wet seasons (Tables 3a and b). Lead had concentration below background value in wet season soil.

Table 3a: Igeo of dry season soil samples.

Heavy metals (mg/l)	Sample Locations											Average Igeo
	OK03	OK06	OK08	OK10	OK11	OK12	OK16	OK17	OK18	OK19	OK20	
Fe	0.76	1.97	1.11	0.65	-0.42	0.59	-0.38	0.21	-0.54	0.70	-0.45	**0.38**
Cu	1.82	1.29	-0.23	0.42	-0.11	0.10	2.28	1.10	-0.23	1.03	0.80	**0.75**
Zn	0.20	1.56	1.10	0.45	-0.88	1.09	1.05	1.25	-0.23	1.11	1.12	**0.71**
Pb	2.77	2.26	2.71	3.65	2.55	2.79	3.18	2.85	2.77	2.09	2.34	**2.72**
Ni	1.55	2.18	2.11	1.38	2.17	1.50	2.08	1.97	1.55	0.18	0.02	**1.52**
Cd	0.24	0.59	-0.04	0.68	-0.01	-0.22	0.50	0.26	-0.04	-0.54	-2.13	**1.42**

Source: Ameh, *et al.*, 2014

Based on the Igeo average, Fe, Cu, and Zn were < 1 in dry season soil. This means that the soil was unpolluted with respect to these metals. However, on a sample location by sample location basis, some of these metals revealed moderately to unpolluted at some points (Table 3a). Nickel and Cd had average Igeo values of between 1 and 2, that is moderately to unpolluted. Of all the metals under investigation in dry season soil, Pb had the highest average Igeo of 2.72. This value of 2.72 implies moderately polluted soil as far as Pb is concern in the area (Table 3a).

In wet season soil sample results, the average Igeo for Cu, Zn and Pb were <0. This value suggest less than background concentration of these metals in the soil

Table 3b: Igeo of Okaba wet season soils.

Sample Location	Heavy metals(mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
OK21	0.43	-2.12	-1.36	-1.06	-2.56	5.67
OK22	2.13	-2.40	0.75	-1.06	3.37	6.09
OK29	0.91	-2.56	-0.30	-2.06	3.87	5.99
OK30	1.66	-5.88	-0.25	-4.06	3.14	4.81
OK31	1.49	-0.92	-0.03	-0.45	2.84	5.93
OK32	1.43	-0.97	-0.14	0.48	2.91	5.74
OK33	1.75	-2.56	0.10	-2.06	3.32	4.72
OK34	2.10	-1.40	0.81	-0.45	3.27	6.07
OK37	1.72	-1.56	0.19	-2.47	3.06	4.70
Average Igeo	**1.5**	**-2.26**	**-0.35**	**-1.57**	**2.58**	**5.52**

Table 4a: Enrichment factor (EF) of heavy metals in dry season soils.

Heavy Metals	Sample locations											Average EF
	OK03	OK06	OK08	OK10	OK11	OK12	OK16	OK17	OK18	OK19	OK20	
Fe	1.48	1.33	1.00	1.15	2.77	0.71	0.32	0.49	0.81	0.75	0.34	**1.01**
Cu	2.07	0.63	0.4	0.85	1.23	0.71	6.29	1.86	1.24	1.26	2.38	**1.72**
Zn	0.68	0.75	1.00	0.87	0.36	1.41	2.69	2.06	1.24	1.33	2.97	**1.40**
Pb	4.01	1.23	3.04	7.98	7.79	4.61	11.75	6.22	9.86	2.63	6.92	**6.00**
Ni	1.73	1.16	2.00	1.64	5.98	1.89	5.50	3.40	4.25	0.70	1.39	**2.69**
Cd	0.70	0.38	0.45	1.02	1.32	0.57	1.83	1.04	1.41	0.42	0.31	**0.86**

Source: Ameh, *et al.*, 2014

The average dry season enrichment factor of metals in soil indicated that Fe, Cu and Zn have depletion to minimal enrichment in soils (Sutherland, 2000). Cadmium recorded background concentration (EF=0.86) in soil while Ni was moderately enriched. Lead (Pb) recorded the highest EF of 6.00 which is an indication of significant enrichment in soil (Table 4a). In wet season soil, Cu, Zn and Pb had average EF of below 1.0 which shows background concentration of these metals in wet season soil. This indicates moderate soil enrichment (Table 4b). The highest EF of 18.76 was recorded by Cd in the wet season soils. This implies that the soil was significantly enriched with Cd (Table 4b).

Using EF as the fulcrum of comparison, Cu and Zn recorded lower EF in wet season (background concentration) but in the dry season, their concentrations in soil were depletion to minimal enrichment. Nickel in both seasons recorded moderate enrichment, though actual wet season value was slightly higher. Cadmium showed contrasting characteristics in both seasons. In wet season, Cd showed significant enrichment in soil and background concentration in dry season. The EF as observed with Igeo had shown seasonal variations in soils with respect to these metals (Tables 4a and b).

Table 4b: Enrichment factor (EF) of Okaba wet season soils.

Sample Location	Heavy metals (mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
OK21	3.51	0.20	0.28	0.36	0.12	37.65
OK22	2.59	0.04	0.39	0.11	2.37	15.65
OK29	2.33	0.09	0.43	0.13	7.79	33.80
OK30	3.74	0.01	0.27	0.02	2.81	8.90
OK31	2.86	0.19	0.35	0.26	2.55	21.67
OK32	2.94	0.19	0.34	0.52	2.79	19.85
OK33	3.14	0.05	0.32	0.07	2.98	7.84
OK34	2.45	0.09	0.41	0.17	2.25	15.57
OK37	2.89	0.10	0.35	0.06	2.53	7.90
Average EF	**2.94**	**0.11**	**0.35**	**0.19**	**2.91**	**18.76**

Another index used to determine the degree of soil pollution and seasonal variation by metals arising from coal mining activities was contamination factor (CF). From the average dry season soil EF values, Fe, Cu, Zn and Cd revealed moderate contamination (1≥ CF ≥3). The dry season soil also experienced considerable contamination (3≥CF≥6) with respect to Ni (Table 5a). Lead (Pb) on the other hand recorded the highest value of 10.35 (CF>6), which signifies very high contamination level of Pb in soil (Table 5a). The CF of metals in wet season soil revealed low contamination (CF<1) of soil with respect to Cu and Pb while Zn recorded 1.6 CF (moderate contamination) in soil, 4.53 (considerable contamination) CF was revealed in soil by Fe. For the same wet season, Ni and Cd recorded CF values of 12.78 and 74.11 respectively. These values indicate very high contamination of both metals in the soil (Table 5b).

In terms of metal variations in both seasons, Ni and Cd indicated very high contamination in wet season while considerable contamination and moderate contamination respectively were observed in dry season of same soil for Ni and Cd. This means higher concentration of Ni and Cd in soil in wet season. In the dry season soil, Fe, Cu and Zn showed moderate contamination. In wet season, Fe content in soil was higher (CF=4.53), considerable contamination, Cu showed low contamination (CF<1) and Zn indicated moderate soil contamination (CF=1.6). The CF has also shown that there were variations of metal content in soil between the seasons (Tables 5a and b).

Metal Concentrations in Sediment in both Seasons

From table 6a, Fe has the highest mean concentration values of 608.03mg/l, followed by Na (115.97mg/l), K (31.0mg/l) and Ca (29.36mg/l) in dry season sediments. The least mean concentration values among the toxic metals were Pb (0.56mg/l) and the highest was Ni (2.8mg/l). In wet season sediments (Table 6b), the mean

Table 5a: CF of heavy metals in Okaba dry season soils

Heavy Metals (mg/l)	Sample Locations											Average CF
	OK03	OK06	OK08	OK10	OK11	OK12	OK16	OK17	OK18	OK19	OK20	
Fe	2.55	5.87	3.23	2.35	1.13	2.26	1.16	1.74	1.03	2.43	1.10	**2.26**
Cu	5.28	3.67	1.28	2.00	1.39	1.61	7.28	3.22	1.28	3.06	2.61	**2.97**
Zn	1.72	4.43	3.22	2.06	0.41	3.19	3.11	3.57	1.28	3.24	3.26	**2.68**
Pb	10.2	7.20	9.80	18.8	8.80	10.4	13.6	10.8	10.20	6.40	7.60	**10.35**
Ni	4.40	6.78	6.47	3.90	6.76	4.26	6.36	5.90	4.40	1.70	1.52	**4.77**
Cd	1.77	2.26	1.46	2.40	1.49	1.29	2.11	1.80	1.46	1.03	0.34	**1.58**

Source: Ameh, *et al.*, 2014

Table 5b: Contamination factor (CF) of Okaba wet season soils.

Sample Location	Heavy Metals(mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
OK21	2.03	0.41	0.58	0.73	0.25	76.5
OK22	6.55	0.28	2.53	0.73	15.5	102.5
OK29	2.83	0.26	1.21	0.36	22	95.5
OK30	4.72	0.03	1.26	0.09	13.25	42
OK31	4.22	0.79	1.47	1.09	10.75	91.5
OK32	4.03	0.77	1.37	2.09	11.25	80
OK33	5.04	0.26	1.61	0.36	15	39.5
OK34	6.45	0.56	2.63	1.09	14.5	100.5
OK37	4.94	0.51	1.71	0.27	12.5	39
Average CF	**4.53**	**0.43**	**1.60**	**0.76**	**12.78**	**74.11**

concentration of Fe (164.12mg/l) was the highest among the metals, followed by K (29.25mg/l); Ca (23.48mg/l) and Na (16.22mg/l).The least among the toxic metals were Pb (0.06mg/l) and the highest was Cd (1.12mg/l). Comparing both seasons, Mg and Cd increased in wet season compared to dry season. Sodium and Fe on the other hand revealed significant reduction in concentration between the seasons (Table 6b).

The clay was the most dominant sediment fraction. This is followed by silt and sand. The pH was acidic with organic matter content of 10% (Table 7).

Table 6a: Summary statistics of Okaba dry season sediments (mg/l).

Variables	Minimum	Maximum	Mean	Std. Deviation	t-square	95% Confidence Interval Difference Lower	Upper	Average control point value
Na	108.74	124.67	115.9725	6.25331	52.455	110.7446	121.2004	34.27
K	20.50	59.00	31.0875	13.54293	6.493	19.7653	42.4097	17.20
Ca	21.00	41.25	29.3638	6.40684	12.963	24.0075	34.7200	25.22
Mg	.21	6.66	4.0275	2.16009	5.274	2.2216	5.8334	4.43
Fe	362.00	860.12	608.0338	183.42158	9.376	454.6895	761.3780	104.00
Cu	.47	5.16	2.5413	1.92730	3.729	.9300	4.1525	.18
Zn	1.36	4.26	2.8113	.98483	8.074	1.9879	3.6346	.65
Pb	.19	.76	.5550	.19369	8.105	.3931	.7169	.02
Ni	1.42	5.46	2.8000	1.29178	6.131	1.7200	3.8800	.92
Cd	.14	1.80	.7850	.54071	4.106	.3330	1.2370	.56

Source: Ameh, *et al.*, 2014

Table 6b: Summary statistics of Okaba wet season sediments (mg/l)

Variables	Minimum	Maximum	Mean	Std. Deviation	t- square	95% Confidence Interval of the Difference Lower	Upper	Average control point value
Na	13.82	17.66	16.2170	1.07861	47.545	15.4454	16.9886	22.24
K	3.66	72.24	29.2490	26.41467	3.502	10.3531	48.1449	38.66
Ca	19.25	33.22	23.4750	5.43719	13.653	19.5855	27.3645	29.43
Mg	2.89	3.99	3.2090	.31939	31.772	2.9805	3.4375	2.85
Fe	58.25	451.50	164.1160	113.15372	4.587	83.1707	245.0613	202.80
Cu	.01	.40	.1370	.12275	3.529	.0492	.2248	.12
Zn	.09	1.02	.5400	.31693	5.388	.3133	.7667	.85
Pb	.03	.08	.0550	.02068	8.409	.0402	.0698	.04
Ni	.02	1.32	.5480	.40947	4.232	.2551	.8409	.02
Cd	.31	1.88	1.1160	.50458	6.994	.7550	1.4770	.10

Ecological Indices in Sediment

The sediment samples were also profiled to determine the level of pollution from mining using the same indices as with soil samples.

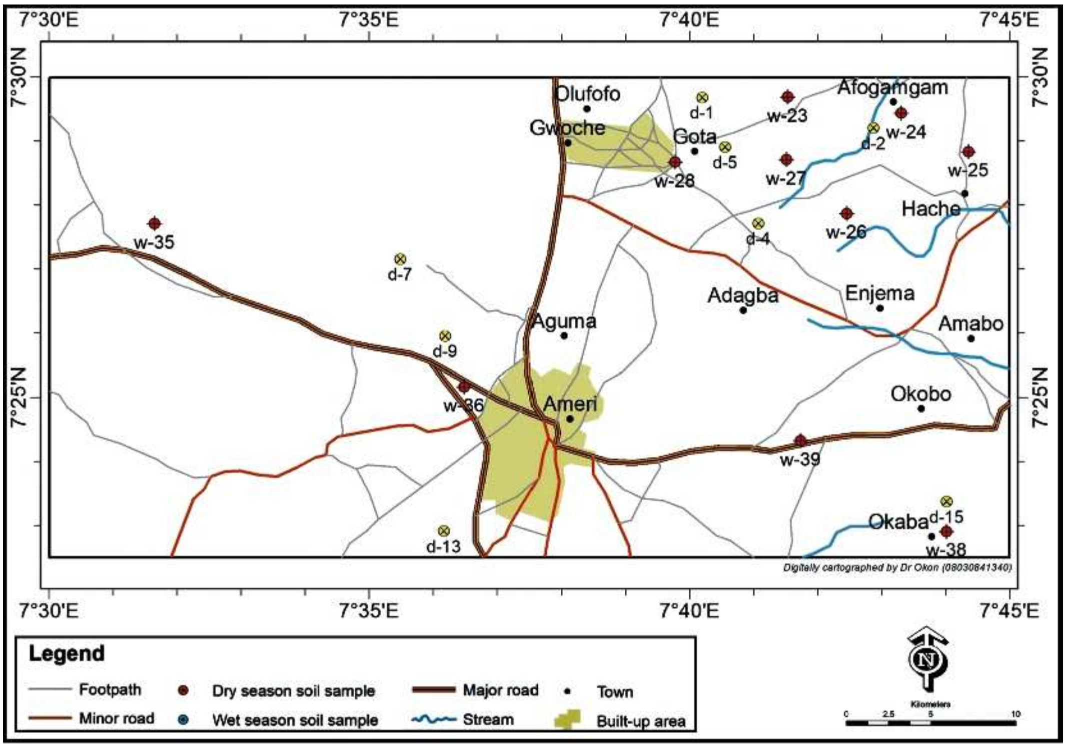

Fig. 3: Sediment sample map.

The Igeo average of dry season sediments concentration indicate that Cd (Igeo = -0.48) was below background level while the sediment was unpolluted with respect to Ni (Igeo =0.89). The Fe and Zn recorded average Igeo values of 1.9 and 1.44 respectively. These showed moderately to unpolluted sediment. The sediment was moderately polluted with Cu (Igeo =2.70). The highest Igeo of 4.10 (highly polluted) was recorded for Pb in the sediments (Table 8a). In wet season, Fe, Cu, Zn and Pb recorded Igeo values less than zero. These means the degree of pollution of soil with these metals was below background value of zero. Cadmium in the same sediment polluted the soil moderately with Igeo value of 2.73 (Table 8b). The highest degree of soil pollution was established with respect to Ni in wet season sediments with Igeo value of 3.55 (moderately to highly polluted).

Table 7: Average sediment properties in Okaba coal mine

Sand %	23.70
Cay %	46.13
Silt%	30.17
Ec	3.64
pH	4.02
OM%	10.08
Temperature	26°C

Table 8a: I_{geo} of heavy metals from Okaba dry season sediments.

Heavy Metals									Average Igeo
Fe	1.96	1.21	1.29	1.96	2.43	2.46	2.06	1.83	**1.90**
Cu	1.03	2.65	3.59	3.90	4.26	4.06	0.80	1.29	**2.70**
Zn	0.48	1.86	1.02	1.68	2.13	1.90	1.17	1.29	**1.44**
Pb	4.44	4.06	4.37	4.44	4.57	4.66	2.66	3.59	**4.10**
Ni	1.98	0.49	1.00	1.09	1.17	1.24	0.04	0.14	**0.89**
Cd	-2.59	0.21	-0.30	-0.56	-0.28	0.53	1.10	-1.93	**-0.48**

Source: Ameh, *et al.*, 2011

Between the two seasons, using Igeo, Ni, and Cd were significantly enriched in wet season sediments than in dry season sediment. On the other hand, Fe, Cu, Zn and Pb were enriched in the sediment more in dry season than in wet season (Tables 8a and b).

Table 8b: Igeo of heavy metals in Okaba wet season sediments.

Sample Location	Heavy metals (mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
OK23	-1.47	1.15	-1.03	-1.00	5.03	3.17
OK24	-0.97	-0.17	-0.58	0.41	3.70	2.30
OK25	0.57	-0.71	-0.81	-1.00	4.52	2.75
OK26	-2.40	-4.06	-3.84	-0.58	1.88	3.44
OK27	-1.51	-2.18	-0.32	0.41	4.74	2.91
OK28	-0.74	-0.43	-1.69	-0.58	-0.58	2.36
OK35	-1.47	-0.47	-1.60	0.41	4.27	3.64
OK36	-2.12	-1.84	-3.47	-0.27	5.46	1.05
OK38	-0.64	-1.18	-1.89	-0.27	3.70	3.46
OK39	-0.56	-1.00	-0.64	0.23	2.74	2.20
Average Igeo	**-1.13**	**-1.09**	**-1.59**	**-0.23**	**3.55**	**2.73**

The contamination factor (CF) is another index used for the determination of sediment pollution. Cadmium has the least average contamination of 1.40 in dry season sediment (moderate contamination) while Pb had the highest CF value of 27.75 (very high contamination). The dry season sediment experienced considerable contamination (3≥ CF≥ 6) with respect to Fe, Zn and Ni (Table 10a). The degree of pollution on soil from Cu was also very high (CF>14). In wet season for the same sediment, Fe and Zn recorded CF<1, this is low sediment contamination. The sediment also recorded average CF of 1.14 and 1.38 respectively for Cu and Pb (moderate contamination). However, average Ni and Cd

Table 9a: Enrichment factor (EF) of Okaba dry season sediments.

Heavy Metals (mg/l)	Sample locations								Average EF
	OK01	OK02	OK04	OK05	OK07	OK09	OK13	OK15	
Fe	2.79	0.64	1.20	1.22	1.24	1.47	1.86	1.45	**1.48**
Cu	0.52	2.69	4.94	3.84	3.54	3.03	0.42	0.69	**2.46**
Zn	0.36	1.56	0.83	0.82	0.81	0.68	0.54	0.69	**0.79**
Pb	5.57	7.18	8.48	5.57	4.38	4.59	1.52	3.37	**4.07**
Ni	1.02	0.61	0.82	0.55	0.42	0.43	0.25	0.31	**0.55**
Cd	0.04	0.50	0.33	0.17	0.15	0.26	0.51	0.07	**0.25**

The Igeo average of dry season sediments concentration indicate that Cd (Igeo = -0.48) was below background level while the sediment was unpolluted with respect to Ni (Igeo =0.89). The Fe and Zn recorded average Igeo values of 1.9 and 1.44 respectively. These showed moderately to unpolluted sediment. The sediment was moderately polluted with Cu (Igeo =2.70). The highest Igeo of 4.10 (highly polluted) was recorded for Pb in the sediments (Table 8a). In wet season, Fe, Cu, Zn and Pb recorded Igeo values less than zero. These means the degree of pollution of soil with these metals was below background value of zero. Cadmium in the same sediment polluted the soil moderately with Igeo value of 2.73 (Table 8b). The highest degree of soil pollution was established with respect to Ni in wet season sediments with Igeo value of 3.55 (moderately to highly polluted).

Table 9b: Enrichment factor (EF) of Okaba wet season sediments.

Sample Location	Heavy Metals (mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
OK23	0.72	6.25	1.39	1.41	92.01	25.35
OK24	0.76	1.75	1.32	2.63	25.66	9.74
OK25	2.59	0.41	0.39	0.34	15.50	4.54
OK26	2.71	0.29	0.37	3.48	19.15	56.75
OK27	0.43	0.64	2.31	3.85	76.98	21.75
OK28	1.96	2.78	0.51	1.11	1.11	8.56
OK35	1.10	2.00	0.91	3.69	53.47	34.66
OK36	2.69	1.20	0.37	3.60	189.85	8.92
OK38	2.33	0.69	0.43	1.30	20.32	17.19
OK39	1.07	0.74	0.94	1.72	9.83	6.78
Average EF	**1.64**	**1.68**	**0.89**	**2.31**	**50.39**	**19.42**

Table 10a: The CF of heavy metals in Okaba dry season sediments

Heavy Metals (mg/l)	Sample Locations								Average CF
	OK01	OK02	OK04	OK05	OK07	OK09	OK13	OK15	
Fe	5.84	3.48	3.69	5.84	8.10	8.27	6.25	5.34	**5.48**
Cu	3.06	9.39	18.06	22.44	28.7	25.06	2.61	3.67	**14.12**
Zn	2.09	5.45	3.05	4.8	6.55	5.62	3.37	3.68	**4.33**
Pb	32.5	25.00	31.00	32.5	35.5	38.00	9.50	18.00	**27.75**
Ni	5.93	2.11	3.00	3.20	3.37	3.54	1.54	1.65	**3.04**
Cd	0.25	1.73	1.21	1.02	1.23	2.16	3.21	0.39	**1.40**

Source: Ameh, *et al.*, 2011

content in sediment were very high (CF>6). These suggest very high contamination of these metals in sediment (Table 10b).

Looking at both seasons, the sediment experienced very high contamination with regard to Ni and Cd in wet season. In dry season, the sediment revealed considerable contamination with Ni and Cd, the impact was moderate contamination (Tables 10a and b). In dry season sediments, Cu and Pb recorded very high contamination but moderate contamination in wet season. Wet season impact of Fe and Zn were described as low contamination but in dry season considerable contaminations were observed (Tables 10a and b). This index and indeed all indices used so far suggest various degrees of variation of the metals between the seasons.

Table 10b: Contamination factor (CF) of Okaba wet season sediments.

Sample Location	Heavy Metals (mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
OK23	0.53	3.33	0.74	0.75	49	13.5
OK24	0.76	1.33	1.00	2.00	19.5	7.40
OK25	2.23	0.92	0.86	0.75	34.5	10.1
OK26	0.29	0.08	0.11	1.00	5.50	16.3
OK27	0.52	0.33	1.20	2.00	40	11.3
OK28	0.90	2.50	0.46	1.00	1.00	7.70
OK35	0.54	1.08	0.49	2.00	29	18.8
OK36	0.35	0.42	0.13	1.25	66	3.10
OK38	0.96	0.67	0.41	1.25	19.5	16.5
OK39	1.02	0.75	0.95	1.75	10	6.90
Average CF	**0.81**	**1.14**	**0.64**	**1.38**	**27.4**	**11.16**

Discussion

The potential for acid mine drainage and the release of toxic metals from mine wastes exist throughout Okaba coal mine area. Previous works have shown that toxic metals such as As, Co, Cu,Ni, Cr, Pb Zn, Cd etc were present in coal mine area (*Lyons et al., 1989*). *Adaikpoh et al., 2005* also confirm the presence of toxic metals such as Pb, Cd, Ni, Cu, Zn etc in Enugu coal mining area. Based on the three indices (Igeo, EF and CF) used in this study, Pb , Ni and Cd have polluted the soil, moderately and moderately to unpolluted with respect to the dry season Igeo. For EF and CF, the soil experienced very highly polluted (Ni), moderately polluted with Cd and Fe was moderately to unpolluted for EF index. The CF result showed Pb (significant enrichment), Ni (moderately enriched) while Cu, Zn and Fe revealed depletion to minimal enrichment. The acidic nature of the environment, the reducing environment, the presence of sulphur and subsequent formation of sulphides and the easily weathered nature of these toxic metals on exposure contributed to their high concentrations in the dry season soils (*Scott et al., 1994*). Apart from these reasons above, the metals were released to the environment due to pyrite minerals and base metal deposits (Nelson, 2004). In wet season soil, Cd, Ni, and Fe recorded elevated concentrations than in dry season (Tables 3b, 4b and 5b) for the three indices used. The elevated level of Fe may be due to co-precipitation effect of iron. It could also suggest that Cd, Ni and Fe were among toxic metals not trapped in the hard pan layers and so were readily released in wet season. Cadmium elevation (Tables 3b, 4b and 5b) may also be as a result of its association with sphalerite which is readily weathered and dispersed (*Scott et al., 1994*). The lower concentration of Pb and Cu in wet season soil was as a result of their lower mobility when compared to Fe and Cd (Fagbote and Olanipekun, 2010).

Fine fraction of sediment acts as sink for toxic metal accumulation (*Tijani et al., 2004*). The relative enrichment of these metals (Pb, Cu and Fe) could be associated with sulphides minerals in coal. Other reasons for metal enrichment include acid mine drainage, aerobic oxidation of sulphide minerals (*Thomas, 2002*). Using Igeo, EF and CF indices, the dry season and wet seasons showed the same order of sediment enrichment with these metals. The highest values of concentration of Pb (Tables 8a, 9a and 10a) with respect to all the indices in dry season sediment could be attributed to the sulphide, its strong affinity for sediments and suspended particles and as such strongly sorbed to the sediments (*Eze Chukwu, 2011*).

In wet season sediments, the order of concentration was same among the indices. Iron (Fe) was lower (Tables 8b, 9b and 10b) in wet season than dry season because of oxidation, hydrolysis and rapid precipitation which explain the yellow-red ferric precipitates in stream channels (*Christine and Emily, 2008*). Also, the lower concentrations of Cu, Fe and Zn compared to dry season sediment may also be attributed to higher mobility, adsorption and dispersion during rainfall. The observed higher Ni, and Cd concentrations in wet season sediment using all the indices suggests leaching out of metals into stream sediments and toxic metal transport on suspended sediments which increases during high flow periods (*John et al., 1995*; *Joseph. 1986*). Comparing both seasons, Pb was lower in wet season. This suggests formation of insoluble Pb sulphates when exposed to the atmosphere and thus restrict its dispersion (*John et al., 1995*).

Comparing dry and wet season soils, Ca and Na were lower in wet season soils than dry seasons. Potassium and Mg on the other hand showed higher concentrations in wet season than in dry season (Tables 1a and b). These relatively higher concentrations of K and Mg in wet season may be due to increased mobilization (*Aitta et al., 2019*). Metals, including toxic ones generally have lower concentrations in wet season than in dry season because of the effect of dilution from rainfall. Other metals showed lower concentrations in soils during wet season than dry season due largely to dispersion of the metals over extensive area during runoff (*Navarro et al., 2008; Yahaya et al., 2009*). Cadmium concentration was higher in wet season than dry season in soils as established by the three indices. This increase can be attributed to higher pH values, solubility and increased mobility (*Yahaya et al., 2009*).

The seasonal variations were calculated using Igeo index, enrichment factor and contamination factor indices. From the Igeo index average, Cd, Ni and Fe were higher in wet season than in dry season soil. The Zn, Pb and Cu were on the other hand higher in concentrations in dry season than in wet season (Tables 3a, 4a and b). The enrichment factor and contamination factor averages also showed that Cd, Ni and Fe concentrations were higher in wet season than in dry season while dry season soil concentrations of Pb, Zn and Cu were higher than in wet season (Tables 3a to 5a). These higher concentrations of Zn, Pb and Cu in dry season soil could be due to enrichment of the sampled media in dry season as a result of intense evaporation, their association with sulphide minerals found and released during coal mining. They (Zn, Pb and Cu) were also often broken down easily and released as a result of aerobic oxidation of sulphide minerals (Thomas, 2002; *Yahaya et al., 2009*). Lead (Pb) in particular is immobile and as such remains in soil solution and thus accounted for its lower concentration during rainfall.

From the three indices used also, the concentration of Cd, Ni and Fe were higher in wet season sediment than in dry season (Tables 3b to 5b). These increase in wet season could be attributed to leaching out of these metals and transport on suspended soil. Apart from above general reasons, Fe form Fe-hydroxides and later precipitate under oxidizing conditions (*John et al., 1995*). The Zn and Cu were more mobile and easily carried by runoff and dispersed during rainfall. This could also explain their relatively lower concentration in wet season than in dry season (Harikumar and Jisha, 2010; Reza and Singh, 2010).

Conclusion

Coal mining activities has polluted both soil and sediments in the study area as showed by all the indices used. In general, soils and sediments at dry season showed higher metal concentrations than in wet season. Lead (Pb) consistently showed its immobile characteristics. Iron (Fe), Cd and Ni were on the other hand higher in wet seasons than dry season.

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